

*A Contribution to the Thermodynamical Theory of Explosions.—*

## PARTS I AND II.

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*Introduction.*

The following paper deals with the application of the fundamental ideas of modern physical chemistry to the science of internal ballistics, and aims at eliminating some of the empirical methods and the arbitrary assumptions which have been necessary in the practice and theory of that science in the past. The object of the science is the calculation of the pressure and temperature of the products of explosion throughout the motion of the projectile along the bore of the gun, both during the burning of the propellant and after the burning is completed. It is necessarily a branch of physical chemistry, since it implies a knowledge of the composition of the products of explosion and the variation of these products with temperature, also a knowledge of the variation of the specific heats of gases with temperature. Hence every advance in our knowledge of these branches of physical chemistry will enable a further step to be made in the science of internal ballistics.

To cover our ignorance in this respect it has been customary in internal ballistics to make arbitrary assumptions as to the connection between pressure and volume behind the projectile in the gun. The assumption made for example by Mansell and Hadcock\* is that the equation,  $p(v-b)^n/z^n = \text{constant}$ , is satisfied, the value of  $n$  being different during burning and after burning is completed,  $z$  being the fraction of the charge already burnt.

The present paper makes no assumption of this kind, but contains an application to the problems of internal ballistics of the recent advances in the thermodynamics of dissociation and in the thermodynamics of the variation of specific heats of gases with temperature, with the result that the whole indicator diagram of the gun can now be calculated from the chemical composition of the propellant, combined with a table of heats of formation from the elements of the propellant and its products, and one set of laboratory experiments to determine the rate of burning of the solid propellant and its variation with pressure. Physical chemistry is not yet sufficiently advanced to enable this rate to be calculated.

Part I contains the calculations of the maximum temperature and pressure

\* A good review of previous work is given by Sir George Hadcock, F.R.S., in his paper on Internal Ballistics, 'Roy. Soc. Proc.,' A, vol. 94 (1917).

for an explosion in a closed vessel, also the calculation of the curve of reversible adiabatic expansion of the products and incidentally the ideal indicator diagram. This part was written in 1913-14 and publication was then prohibited.

Part II was written in 1915-16 and contains the calculations for the gun, in which the variation with time of the volume of the chamber, of the composition of the products and of the temperature and pressure of explosion, are all worked out point by point and the value of the maximum pressure is determined.

This complete theory was put to very severe test by application to many practical problems during the War, made by that distinguished scientific artilleryman, Captain Maxwell Lefroy, R.N., member of the Ordnance Committee, with very satisfactory agreement between theory and practice. Incidentally it may be noted that since actual direct experiments on specific heats of gases have been limited to temperatures below 1500° C. and pressures of a few hundred pounds per square inch, whereas in ballistics temperatures of 3500° C. and pressures of 20 Tons/in.<sup>2</sup> are common, the application to ballistics of the theoretical thermodynamical equations forms a severe test of the theory.

PART I.—*The Calculation of the Temperature of Explosion, the Curve of Adiabatic Expansion, with Special Reference to the Explosion of Cordite and the Ideal Indicator Diagram.\**

By Sir J. B. HENDERSON, D.Sc.

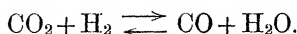
The general theory will be illustrated by an example of its application to the explosion of Mark I. cordite, and the results for M.D. cordite are added, but it will be understood that the method is equally applicable to any propellant.

$$\left. \begin{array}{l} 1 \text{ grm. of } \\ \text{Mark I. } \\ \text{cordite} \end{array} \right\} = \left\{ \begin{array}{ll} 0 \cdot 37 \text{ grm. guncotton} \\ 0 \cdot 58 \text{ " nitroglycerine} \\ 0 \cdot 05 \text{ " vaseline} \end{array} \right. = \left\{ \begin{array}{ll} 0 \cdot 2308 \text{ grm. carbon} \\ 0 \cdot 0300 \text{ " hydrogen} \\ 0 \cdot 1553 \text{ " nitrogen} \\ 0 \cdot 5837 \text{ " oxygen} \end{array} \right. = \left\{ \begin{array}{llll} 0 \cdot 01924 \text{ grm. atom of C.} \\ 0 \cdot 0300 \text{ " " H.} \\ 0 \cdot 0111 \text{ " " N.} \\ 0 \cdot 0365 \text{ " " O.} \end{array} \right.$$

The products of explosion will contain CO<sub>2</sub>, H<sub>2</sub>, CO, H<sub>2</sub>O and N<sub>2</sub> with possibly small quantities of NH<sub>3</sub>, CH<sub>4</sub>, NO; it is also possible that some of the CO<sub>2</sub> and H<sub>2</sub>O are dissociated, but whatever the composition, it will be assumed that at any temperature the composition represents a state of thermodynamic equilibrium so that the equations for such a state are applicable. We shall first of all neglect the small quantities of NH<sub>3</sub>, CH<sub>4</sub> and NO present, also the dissociation of CO<sub>2</sub> and H<sub>2</sub>O, and prove later that these are negligible. The

\* The author is much indebted for valuable assistance and advice on the chemical side to Dr. Thomas Ewan, of Glasgow.

gaseous reaction which varies with the temperature is then the water-gas reaction



Let  $p, q, r$  and  $s$  be respectively the numbers of gramme-molecules per gramme of products, and let C, O, H and N be the numbers of gramme-atoms of C, O, H and N respectively in the products, then

$$p + q = \text{C}; \quad 2p + q = \text{O}; \quad 2r + 2s = \text{H}; \quad \frac{qs}{pr} = K_c,$$

where 
$$K_c = \frac{[\text{CO}] \times [\text{H}_2\text{O}]}{[\text{CO}_2] \times [\text{H}_2]}.$$

Values of  $\log K_c$  for the water-gas reaction may be obtained from works on physical chemistry.

Since  $K_c$  varies with temperature, it is necessary to assume first of all a value of  $K_c$ , then solve for  $p, q, r$  and  $s$ , and if the values so obtained lead to a value of the temperature considerably different from that associated with the assumed value of  $K_c$ , then the calculations have to be repeated with a new corrected value of  $K_c$ . A large error in  $K_c$ , however, makes a small difference in the products.

Taking  $K_c = 14$  which corresponds to a temperature of  $3400^\circ$  abs.

$p$	=	0.00486	gram.-mols.	per	gram.	cordite.
$q$	=	0.01438	"	"	"	
$r$	=	0.00262	"	"	"	
$s$	=	0.01238	"	"	"	
$\text{N}_2$	=	0.00554	"	"	"	
Sum	=	0.03978	"	"	"	

The characteristic equation for a gas, or mixture of gases, at high temperatures and pressures is  $p(v-b) = R\theta$ , where  $v$  is the specific volume of the products,  $b$  the specific volume of the molecules themselves, which may be taken as the specific volume of the solid explosive. The value of  $R$  for a mixture of gases is the sum of the concentrations of the constituent gases in gramme-molecules per gramme, multiplied by a constant which is 2760 ft. Lbs./lb.  $\times$  deg. C. Hence

$$R = 0.0398 \times 2760 = 109.8 \frac{\text{ft. Lbs.}}{\text{lb.} \times \text{deg. C.}} = 3.25 \frac{\text{atmos.} \times \text{cm.}^3}{\text{gram.} \times \text{deg. C.}}$$

#### *Thermal Values.*

Berthelot has given the heats of formation from the elements of collodion, guncotton, nitroglycerine, vaseline and all the above gases formed in the

explosion, all at 15° C. The heat evolved per gramme of cordite at 15° C. is next calculated from Berthelot's figures combined with the above values of  $p$ ,  $q$ ,  $r$ , etc., which corresponds to the heat evolved in the explosion, or the heat evolved if the gases were cooled from explosion temperature to 15° C. without altering their composition.

	Molecular weight.	Heat of formation per gm.-mol. from elements (at 15° C.).	Heat of formation per gm.
		calcs.	
Collodion, $C_{24}H_{31}O_{38}N_9$ .....	1053	696,000	660
Guncotton, $C_{24}H_{29}O_{42}N_{11}$ .....	1143	624,000	546
Nitroglycerine, $C_3H_5N_3O_9$ .....	227	98,000	432
Vaseline, $C_{20}H_{42}$ (?) .....	282	97,100	344
Carbon dioxide, $CO_2$ .....	44	94,300	
Carbon monoxide, $CO$ .....	28	26,300	
Steam, $H_2O$ .....	18	58,000 }	
Water, $H_2O$ .....	18	68,400 }	

Since the heats of formation are determined at atmospheric pressure, it is necessary, in order to get the heat of formation  $Q_1$  at constant volume, to add the energy which has been expended in doing external work, namely, 550 calories per gramme-molecule of gas produced. Instead of adding this to each item, it will be added at the end of the heat balance.

Hence the heat balance of the explosion of cordite, Mark I, stands as follows, assuming guncotton to be a mixture of 70 per cent. guncotton,  $C_{24}H_{29}N_{11}O_{42}$  and 30 per cent. collodion  $C_{24}H_{31}N_9O_{38}$  :—

Heat absorbed by the decomposition at 15° C. of—

$$\begin{aligned}
 0.7 \times 0.37 \text{ gm. guncotton} &= 546 \times 0.259 = 141.4 \text{ calcs} \\
 0.3 \times 0.37 \text{ „ collodion} &= 660 \times 0.111 = 73.3 \text{ „} \\
 0.58 \text{ gm. nitroglycerine} &= 432 \times 0.58 = 250.5 \text{ „} \\
 0.05 \text{ „ vaseline} &= 344 \times 0.05 = 17.2 \text{ „}
 \end{aligned}$$

$$\text{Sum} = 482.4 \text{ calcs.}$$

Heat evolved by the formation at 15° C. of—

$$\begin{aligned}
 0.00486 \text{ gm.-mol. } CO_2 &= 0.00486 \times 94300 = 458.4 \text{ calcs.} \\
 0.01438 \text{ „ } CO &= 0.01438 \times 26300 = 378.2 \text{ „} \\
 0.01238 \text{ „ steam} &= 0.01238 \times 58000 = 718.5 \text{ „} \\
 0.0398 \text{ „ of gas} &= 0.0398 \times 550 = 21.9 \text{ „}
 \end{aligned}$$

$$\text{Sum} = 1577.0 \text{ calcs.}$$

Hence the total heat evolved per gramme of cordite = 1094.6 calcs.

The heat evolved in cooling the gases from explosion temperature to 15° C. must be equal to 1094.6 calories, whence the temperature of explosion is obtainable if the specific heats of the products are known.

### Specific Heats.

Experimental determination of the specific heats of gases by direct measurement is limited to temperatures below 1500° C., and without a thermodynamic theory of the variation of the specific heats with temperature, further advance in the theory of explosion would be difficult, if not impossible. Such theories are those proposed by Einstein and by Nernst and Lindemann, based upon Planck's quantum theory.

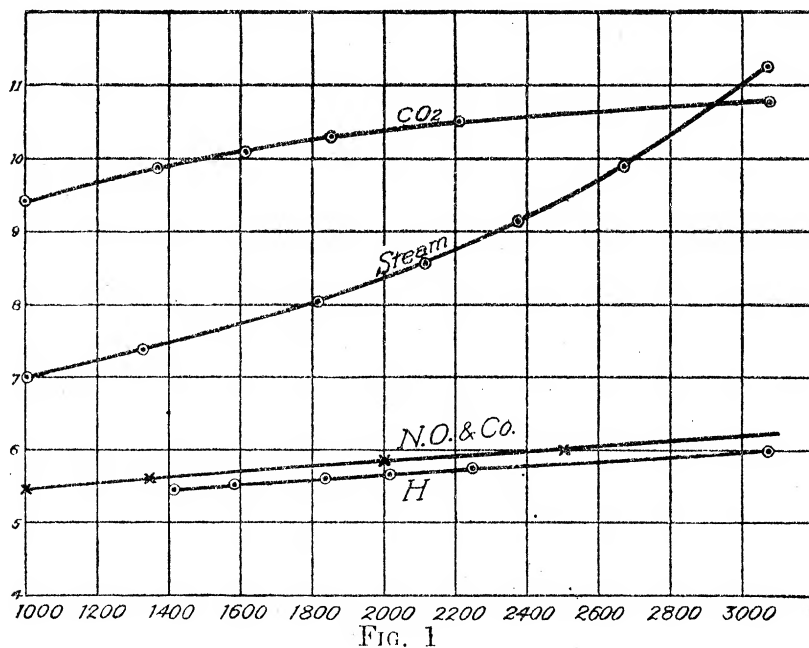


FIG. 1

The curves in fig. 1 show the variation of the specific heats of CO<sub>2</sub>, H<sub>2</sub>O, N, O and H, with temperature as given by Bjerrum, calculated by the Nernst-Lindemann formula

$$\frac{\partial E}{\partial \theta} = \frac{R}{2} \left\{ \frac{x^2 e^x}{(e^x - 1)^2} + \frac{(x/2)^2 e^{x/2}}{(e^{x/2} - 1)^2} \right\} \text{ where } x = \frac{hn}{R\theta}.$$

The following table is prepared from these curves :—

Grm.-mol. of products per grm. of cordite.	$t = 2000^{\circ} \text{C.}$		$t = 2500^{\circ} \text{C.}$		$t = 3000^{\circ} \text{C.}$	
	Mol. heat.	Mol. heat $\times$ grm.-mol. of products.	Mol. heat.	Mol. heat $\times$ grm.-mol. of products.	Mol. heat.	Mol. heat $\times$ grm.-mol. of products.
$\text{CO}_2 = 0\cdot00486 \dots\dots\dots$	10·32	0·0501	10·57	0·0514	10·75	0·0523
$\text{CO} + \text{N}_2 = 0\cdot01992 \dots\dots$	5·77	0·1150	5·94	0·1184	6·15	0·1226
$\text{H}_2 = 0\cdot00262 \dots\dots\dots$	5·62	0·0147	5·78	0·0151	5·95	0·0156
$\text{H}_2\text{O} = 0\cdot01238 \dots\dots\dots$	8·42	0·1042	9·46	0·1171	11·02	0·1365
Heat capacity of products =		0·2840	—	0·3020	—	0·3270

Now, the product heat capacity  $\times$  temperature = heat contents, and the temperature has to be calculated at which this product is equal to the heat evolved in the explosion, namely, 1094·6 calories per gramme of cordite.

Temperature.	Heat capacity.	Product.	Difference.
2000	0·2840	568	—
2500	0·3020	755	187
3000	0·3270	981	226

Plotting the product on a temperature base and reading off the temperature corresponding to a product 1095, we find  $3210^{\circ} \text{C.}$ , or  $3483^{\circ}$  absolute.

In Service Chemistry a simple approximate formula is given for Mark I. cordite:— $\text{C}_5\text{H}_8\text{N}_3\text{O}_{10}$ . If the above calculations are repeated, using this formula the results are:— $p = 0\cdot00572$ ,  $q = 0\cdot01278$ ,  $r = 0\cdot00202$ ,  $s = 0\cdot01278$ ,  $\text{N}_2 = 0\cdot00556$  and  $\text{R} = 3\cdot175$ . The heat evolved by the formation of the products = 1638·2, and, assuming the heat absorbed by the decomposition of the cordite molecule the same as above, viz., 482, the heat balance is 1156·2 and the temperature of explosion is  $3600^{\circ} \text{C.}$  absolute, instead of  $3500^{\circ}$  from Berthelot's composition formulæ.

The calculations have also been repeated for M.D. cordite, containing 65 per cent. guncotton, 30 per cent. nitro-glycerine, and 5 per cent. vaseline, with the following results:— $p = 0\cdot0031$ ,  $q = 0\cdot0184$ ,  $r = 0\cdot0046$ ,  $s = 0\cdot0111$ ,  $\text{N}_2 = 0\cdot0050$ ,  $\text{Sum} = 0\cdot0422$ ,  $\text{R} = 3\cdot44$  (atmos.  $\times$  cm.<sup>3</sup>)/grm.  $\times$  deg. C.). The heat of formation of 1 grm. of M.D. cordite is 524, and the heat balance works out at 913 calories evolved per gramme; and the temperature of explosion is  $2870^{\circ} \text{C.}$ , or  $3143^{\circ} \text{C.}$  absolute, or  $340^{\circ} \text{C.}$  lower than for Mark I.

*Influence of Initial Temperature of Cordite.*

The influence of the initial temperature may be determined as follows:—  
Let the explosion take place at different initial temperatures,  $t_1$  and  $t_2$ , the corresponding temperatures of explosion being  $T_1$  and  $T_2$ . It is easy to imagine the chemical change taking place at  $t_1$  until the products are the same as exist at  $T_1$ , and that the products are then heated up from  $t_1$  to  $T_1$  by the heat evolved. Secondly, imagine that the cordite is heated up from  $t_1$  to  $t_2$  by adding heat  $h$  from external sources, then let the chemical change take place at  $t_2$  until the products are those existing at  $T_2$ , the heat evolved being then used to raise the temperature of the products from  $t_2$  to  $T_2$ . If the heat  $h$  were not supplied from external sources, the final temperature in the second case must be  $T_1$ , since the temperature of explosion is independent of the path followed in the explosion. Hence the heat  $h$  is equal to that required to raise the temperature of the products from  $T_1$  to  $T_2$ , neglecting the small difference in the products at these temperatures, so that

$$\begin{aligned} & (\text{specific heat of solid cordite}) (t_2 - t_1) \\ & = (\text{specific heat of products at constant volume at} \\ & \quad \text{temperature of explosion}) (T_2 - T_1). \end{aligned}$$

Now, the specific heats of solid cordite at ordinary temperatures are 0.365 for Mark I. and 0.347 for M.D., as given by Sir Robert Robertson, and, for the former, the specific heat of the products at the temperature of explosion is 0.372, as calculated from the above theory. Hence the rise in the temperature of explosion is  $0.365/0.372$  of the rise in the temperature of the solid cordite, so that the temperature of explosion is practically increased by an amount equal to the rise of temperature of the solid cordite. For an increase from  $60^\circ$  F. to  $80^\circ$  F., the temperature of explosion is therefore increased by  $20^\circ$  F., or  $11^\circ$  C., which is within the limits of error in the determination of the temperature of explosion itself.

*Pressure of Explosion.*

The temperature of explosion having been determined, the pressure for any particular density of loading follows at once from the characteristic equation. For Mark I. cordite,  $b = 0.641$  cm.<sup>3</sup>/gram., and, if the density of loading be 0.5 gram. per cm.<sup>3</sup> of bomb capacity,

$$p = 8370 \text{ atmos.} = 55.1 \text{ tons/in}^2.$$

*Correction of Results for Dissociation.—Dissociation of CO<sub>2</sub> at 3500° abs. and Pressure of Explosion.*

$$\log_{10} K_c = \log_{10} \frac{[\text{CO}]^2 [\text{O}_2]}{[\text{CO}_2]^2} = -1.6 = \bar{2}.40.$$

With a density of loading 0.5 gm./cm<sup>3</sup>, or 1 gm. per 0.002 litre, the concentrations are at once determined by the composition of the products on p. 463.

$$[\text{CO}_2] = \frac{0.00486}{0.002} = 2.43 \text{ gm.-mols./litre,}$$

$$[\text{CO}] = \frac{0.01438}{0.002} = 7.19 \quad \text{,,} \quad \text{,,}$$

whence  $[\text{O}_2] = 0.00287$ , or 0.0012 gm.-mols. of O<sub>2</sub> per gramme-molecule of CO<sub>2</sub>, and since the dissociation of 2 gm.-mols. of CO<sub>2</sub> give 1 gm.-mol. of O<sub>2</sub>, the percentage of CO<sub>2</sub> dissociated is 0.24. If the density of loading were 0.05 the percentage dissociated would be 2.4.

*Dissociation of Steam.*—Dealing with the H<sub>2</sub>O in a similar manner and taking  $\log K_c = 5.97$ , gives 0.06 as the percentage H<sub>2</sub>O dissociated at a density of loading of 0.5, which is negligible.

In a similar manner we get  $[\text{CH}_4] = 1.3 \times 10^{-6}$  which is negligible. CH<sub>4</sub> is formed in cooling the products.

$$\begin{aligned} [\text{NO}] &= 0.0160 \text{ gm.-mols. per litre.} \\ &= 32 \times 10^{-6} \text{ gm.-mols. per gramme cordite.} \\ &= 0.96 \text{ per cent. of the products of decomposition.} \\ [\text{NH}_3] &= 0.41 \text{ gm.-mols./litre.} \\ &= 0.00082 \text{ gm.-mols. per gramme of cordite.} \\ &= 1.4 \text{ per cent. of the products of decomposition.} \end{aligned}$$

All these are very small as compared with the main products, CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>, and are *negligible where an accuracy* of about 1 per cent. is aimed at. If any of them were not negligible, it would be easy to allow for it by successive approximation.

*Heat Contents of the Products of Explosion and Curve of Adiabatic Explosion.*

The composition of the products, if in chemical equilibrium, depends only on the temperature, and the intrinsic energy in each of the constituents depends also only on the temperature, hence the heat contents of the products of explosion is a function of the temperature only. It is therefore necessary to take an arbitrary datum both for temperature and for composition of products. The datum taken for temperature is 0° C. and the datum for composition is conveniently taken as the composition at 1500° C. abs.

The heat contents is, therefore, the heat evolved in cooling the products to 1500° abs., allowing combination to take place, and then cooling the products further to 0° C. without allowing further combinations to take place. It will be more convenient in tabular work to cool the products to 0° C. without allowing combination to take place and then allow the product to combine at 0° C. until the composition is that corresponding to 1500° abs. The result must be independent of the path followed, since it is a function of the temperature only.

In Table I the composition of the products of Mark I. cordite is given at 1500°, 2000°, 2500°, 3000°, and 3500° abs., each column being calculated by the method given on p. 463. The heat of reaction for water-gas is added, and these figures might be used if the products were imagined to combine at these temperatures to the standard composition before being cooled to 0° C. They are added chiefly to show that a maximum heat of reaction exists at about 2000° abs. This maximum must have a considerable effect in influencing the final composition of the products formed in bomb calorimeters. The heat of reaction at 0° C. is 10,420 calories per gramme-molecule, and its value at any other temperature  $t$  is obtained from the equation

$$Q + t \text{ (mean specific heat of products)} \\ = Q_0 + t \text{ (mean specific heat of the combining gases).}$$

Table I.—Composition of the Products of Combustion of Mark I. Cordite at various Temperatures.

Temp. deg. C. ....	1227°	1727°	2227°	2727°	3227°
Temp. abs. ....	1500°	2000°	2500°	3000°	3500°
K <sub>c</sub> .....	3·71	6·61	9·5	12·6	16·2
CO <sub>2</sub> .....	0·00700	0·00600	0·00542	0·00502	0·00467
CO .....	0·01224	0·01324	0·01382	0·01422	0·01457
H <sub>2</sub> .....	0·00476	0·00376	0·00318	0·00278	0·00243
Steam .....	0·01024	0·01124	0·01182	0·01222	0·01257
N <sub>2</sub> .....	0·00554	0·00554	0·00554	0·00554	0·00554
Sum .....	0·03978	0·03978	0·03978	0·03978	0·03978
Heat of reaction .....	13,342	14,082	13,717	11,866	6,548

Table II contains the results of the calculation of the heat capacity of the products of explosion of Mark I. cordite, the datum of reference being the

Table II.—Heat Capacity of the Products of Explosion of Mark I Cordite, the Datum of Reference being the Products at 1500° absolute cooled to 0° C.

	1500° abs. = 1227° C.		2000° abs. = 1727° C.		2500° abs. = 2227° C.		3000° abs. = 2727° C.		3500° abs. = 3227° C.	
	Grm.-mols. per grm. of products.	$k_m^*$ 0°- $t^{\circ}$ C. Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m^*$ 0°- $t^{\circ}$ C. Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m^*$ 0°- $t^{\circ}$ C. Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m^*$ 0°- $t^{\circ}$ C. Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m^*$ 0°- $t^{\circ}$ C. Heat contents due to cooling.
CO <sub>2</sub> ...	0·00700	9·69	0·00500	10·16	0·00542	10·46	0·00502	10·7	0·00467	10·8
N <sub>2</sub> +CO	0·01778	5·46	0·01878	5·64	0·01936	5·83	0·01976	6·02	0·02011	6·24
H <sub>2</sub> ...	0·00476	5·30	0·00376	5·50	0·00318	5·63	0·00278	5·90	0·00243	6·10
H <sub>2</sub> O ...	0·01024	7·16	0·01124	7·9	0·01182	8·84	0·01222	10·1	0·01257	11·9
Heat contents due to cooling	323·4			476·8				852·4		1097·7
Heat contents due to chemical change	0		10420 × 0·0010 =	10·4	10420 × 0·00158 =	16·5	10420 × 0·00198 =	20·6	10420 × 0·00233 =	24·3
Total heat contents above 0° C.	323·4			487·2				873·0		1122·0

\*  $k_m$  is the mean specific heat between 0° and  $t^{\circ}$  C.

Table III.—Heat Capacity of the Products of Explosion of M.D. Cordite, the Datum of Reference being the Products at 1500° absolute cooled to 0° C.

	1500° abs. = 1227° C.			2000° abs. = 1727° C.			2500° abs. = 2227° C.			3000° abs. = 2727° C.			3500° abs. = 3227° C.		
	Grm.-mols. per grm. of pro-ducts.	$k_{xx}$ 0°-ℓ° C.	Heat contents due to cooling.	Grm.-mols. per grm. of pro-ducts.	$k_{xx}$ 0°-ℓ° C.	Heat contents due to cooling.	Grm.-mols. per grm. of pro-ducts.	$k_{xx}$ 0°-ℓ° C.	Heat contents due to cooling.	Grm.-mols. per grm. of pro-ducts.	$k_{xx}$ 0°-ℓ° C.	Heat contents due to cooling.	Grm.-mols. per grm. of pro-ducts.	$k_{xx}$ 0°-ℓ° C.	Heat contents due to cooling.
CO <sub>2</sub> ...	0·00543	9·69	64·56	0·00434	10·16	76·10	0·00372	10·46	86·66	0·00323	10·7	94·24	0·00291	10·8	101·40
N <sub>2</sub> + CO	0·02108	5·46	141·22	0·02217	5·64	215·90	0·02279	5·83	295·95	0·02328	6·02	382·20	0·02360	6·24	475·20
H <sub>2</sub> ...	0·00696	5·30	45·26	0·00587	5·50	55·74	0·00525	5·68	66·41	0·00476	5·90	76·60	0·00444	6·10	87·40
H <sub>2</sub> O ...	0·00871	7·16	76·52	0·00980	7·90	133·65	0·01042	8·84	205·20	0·01091	10·10	300·50	0·01123	11·9	432·10
Heat contents due to cooling			327·56			481·39			654·22			853·54			1096·10
Heat contents due to chemical change			0	10420 × 0·00109 =		11·36	10420 × 0·00171 =		17·82	10420 × 0·00220 =		22·92	10420 × 0·00252 =		26·26
Total heat contents.....			327·56			492·75			672·04			876·46			1122·36

products at 1500° abs., cooled to 0° C. The total heat contents given in the last line of the Table are represented within 1 per cent. by the equation

$$H = 15.2 + 0.1223\theta + 55.4 \times 10^{-6}\theta^2$$

where H is in calories per gramme of products of explosion.

Table III corresponds to Table II, but refers to M.D. cordite.

#### *Adiabatic Expansion.*

The equation for a reversible adiabatic expansion expresses the fact that the loss of intrinsic energy is equal to the external work done, or

$$p\delta v = -\left(\frac{\partial H}{\partial \theta}\right)\delta\theta = -(0.1223 + 110.8 \times 10^{-6}\theta)\delta\theta,$$

and since  $p(v-b) = R\theta$  it follows

$$\frac{dv}{v-b} = -\frac{d\theta}{R\theta}(0.1223 + 110.8 \times 10^{-6}\theta)$$

whence 
$$\log_e \frac{v-b}{v_1-b} = \frac{0.1223}{R} \log_e \frac{\theta_1}{\theta} + \frac{110.8 \times 10^{-6}}{R}(\theta_1 - \theta),$$

and substituting the values for R we get

$$\log_{10} \frac{v-b}{v_1-b} = 1.552 \log_{10} \frac{\theta_1}{\theta} + 617 \times 10^{-6}(\theta_1 - \theta),$$

which is the equation for adiabatic expansion. It is easily shown that this equation cannot be represented with sufficient accuracy by an equation of the form  $p(v-b)^n = \text{constant}$ , which necessarily involves H being a linear function of  $\theta$ , whereas it is a quadratic function. This latter type of equation could be used for small changes of temperature,  $n$  varying with the temperature according to

$$\frac{R}{n-1} = \frac{dH}{d\theta} = 0.1223 + 110.8 \times 10^{-6}\theta.$$

#### *Results for M.D. Cordite.*

$$H = 14.68 + 0.1323\theta + 52.57 \times 10^{-6}\theta^2.$$

$$R = 3.486 \times 10^{-6} \text{ ergs./gram.} \times \text{deg. C.}$$

$$= 0.0831 \text{ gram. cal./gram.} \times \text{deg. C.}$$

Adiabatic expansion is given by

$$\log_{10} \frac{v-b}{v_1-b} = 1.593 \log \frac{\theta_1}{\theta} + 549 \times 10^{-6}(\theta_1 - \theta).$$

Heat balance = 913 cal./gram.; temperature of explosion = 2870° C. or 340° lower than Mark I.

*Ideal Indicator Diagram and Mechanical Efficiency of a Gun.*

The ideal indicator diagram may be considered as that obtained by a sudden explosion of all the propellant before the projectile begins to move, to be followed by an adiabatic expansion of the products. The maximum pressure obtained in this way is much greater than the gun could stand; hence it is fairer to take the ideal as that obtained by burning the propellant at the maximum working pressure for which the gun is designed, to be followed by adiabatic expansion.

Fig. 2 shows both types of ideal indicator diagram for M.D. cordite, and, in addition, the curve of pressures for irreversible adiabatic expansion, as in throttling, in which no work is done, corresponding to explosions in closed vessels of different capacities; also the ideal indicator diagram assuming an elliptic curve of rise of pressure; also the uniform pressure at which the cordite would just be all burnt at the muzzle of a gun having a ratio of expansion  $v/v_0$  equal to 4·09.

*Mechanical Efficiency of the Gun.*

Taking the mechanical efficiency of a gun as the ratio of the sum of the kinetic energies of the projectile as it leaves the muzzle, due to translation and rotation, to the work represented by the area of the ideal indicator diagram, as calculated above, the following Table is evolved:—

Table of Efficiencies (M.D. Cordite).

Gun.	Density of loading.	Mass of charge.	$V/V_0$ .	Ballistics (experimental).		Thermo-dynamical work.	Total energy of projectile.	Efficiency.
				Maximum pressure.	Muzzle velocity.			
		lbs.		Tons/ins. <sup>2</sup>	ft./sec.	ft. Tons.	ft. Tons.	per cent.
6" Mark VII ...	0·463	28 $\frac{5}{8}$	4·986	16·55	2761	6,237	5,315	85·2
7·5" Mark III...	0·404	54 $\frac{1}{4}$	4·993	17·79	2781	12,400	10,790	87·0
9·2" Mark XI	0·396	128 $\frac{1}{2}$	3·990	17·76	2870	25,990	21,820	84·0
12" Mark X .....	0·401	260	3·954	16·29	2735	50,630	44,340	87·6
13·5" Mark V ...	0·419	297	4·850	18·78	2501	67,610	60,970	90·2

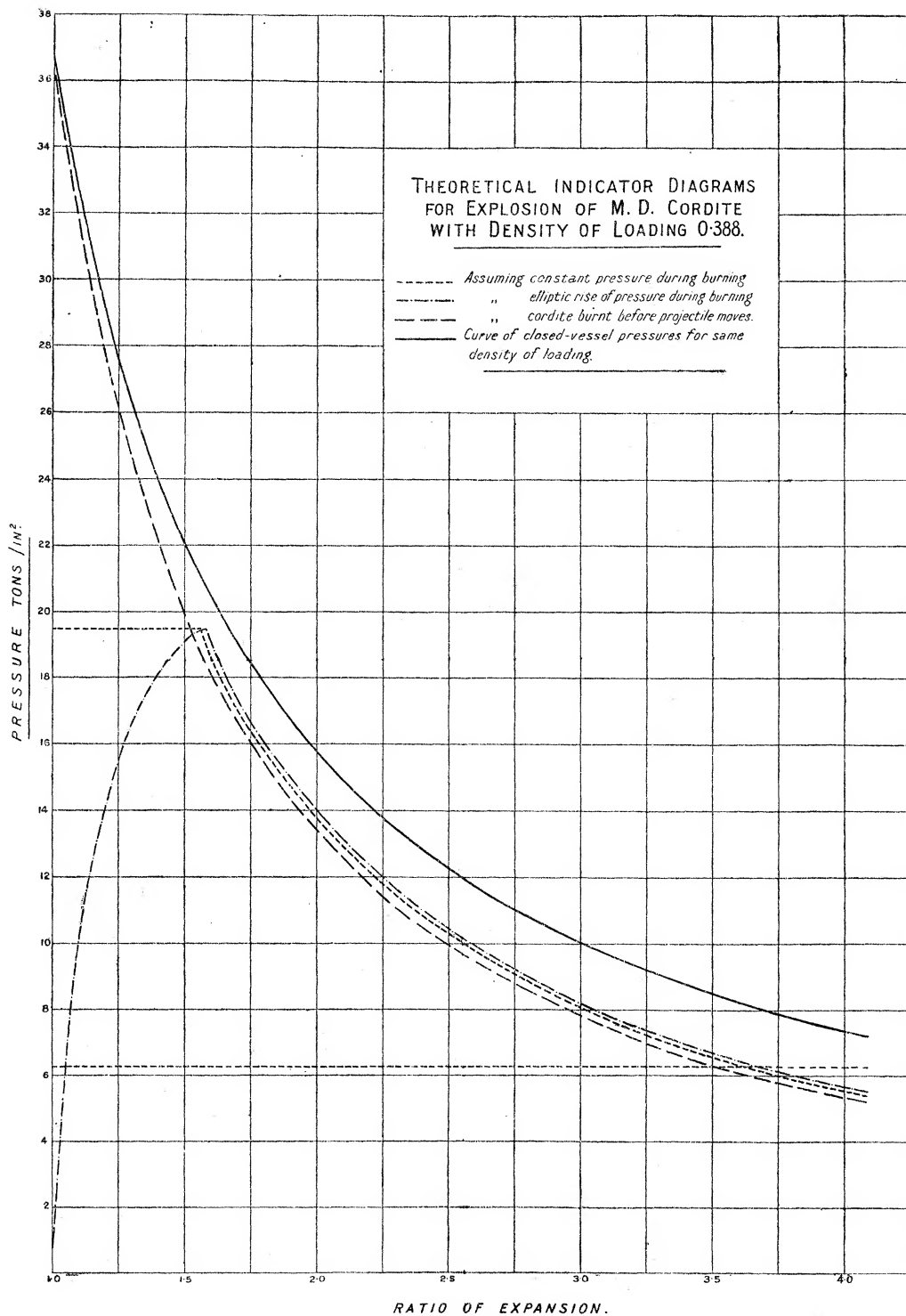


FIG. 2.

PART II.—*The Rate of Rise of Pressure of the Explosion of Cordite in a Gun.—  
The complete Indicator Diagram of the Explosion.*

By Sir J. B. HENDERSON, D.Sc., and Prof. H. R. HASSÉ, D.Sc.

The object of this part of the paper is the application of the results of the thermodynamical theory of Part I to the general problem of Internal Ballistics, the variation of temperature and pressure behind the projectile as it moves along the barrel of a gun. The mathematical theory which follows differs from that given in work previously published,\* in that it is more strictly in accordance with thermodynamical theory; Charbonnier's equations form a special case of the theory, but are not treated in the same way as in the present paper.

The essential features of the theory of Part I of this paper are (1) the determination of the temperature  $\theta_0$  of the explosion; and (2) the expression of the heat contents,  $H$ , of the products of explosion in the form  $\alpha' + \beta'\theta + \gamma'\theta^2$ . The loss of heat contents per unit mass of gas, which measures the work done per unit mass, and is denoted by  $h$ , may therefore be written in the form

$$h = \beta'\theta_0 + \gamma'\theta_0^2 - \beta'\theta - \gamma'\theta^2. \quad (1)$$

For many purposes it is more convenient to express  $\theta_0 - \theta$  as a quadratic function of  $h$ . It is found from (1) that for M.D. cordite the equation

$$\theta_0 - \theta = 3.381h + 20.45 \times 10^{-4}h^2 \quad (1a)$$

will give results in agreement with (1), well within the possible error of (1) as deduced from the theoretical considerations of Part I.

For temperatures differing from that of explosion by less than about  $300^\circ$ ,  $h$  may be expressed as a linear function of  $\theta$  in the form

$$h = f(\theta_0 - \theta), \quad (1b)$$

where for M.D. cordite

$$f = 0.28245 \frac{\text{ft. Tons}}{\text{lb. deg. C.}}$$

*Fundamental Equations of the Theory.*

In formulating these equations, it should be noted: (1) that all forces opposing the motion of the projectile have been neglected; (2) that no attempt has been made to allow for the loss of heat to the walls of the gun; and (3) that it has been assumed that the rate of burning of the propellant depends only on the pressure of the surrounding gas, and is, moreover, proportional to the pressure. The fundamental gas equation is

$$p(V - m_1b) = Rm\theta, \quad (2)$$

\* *E.g.*, the standard work of Charbonnier, 'Balistique Intérieure,' 1908.

$p$  and  $\theta$  being the pressure and temperature of the gas, which has a mass  $m$ ,  $V$  is the volume of the space behind the projectile,  $m_1$  is the total mass of the charge, and  $b$  is the reciprocal of the density of the solid explosive. The theoretical deduction of this equation depends essentially on this interpretation of the constant  $b$ , but the equation may be looked upon as an empirical generalisation of the similar equation, deduced from experimental results in closed vessels, and the value of  $b$  chosen in accordance with these results.\*

If  $M$  is the mass of the projectile,  $u$  its velocity,  $A$  the area of the cross-section of the bore, including that of the grooves, its equation of motion is

$$M \frac{du}{dt} = pA. \quad (3)$$

The scheme of theoretical equations is completed by the equation

$$pdV = d(mh), \quad (4)$$

which expresses the work done by the gases on the projectile in terms of the total loss,  $mh$ , of heat contents at any instant. From these equations, we deduce from (2) and (4) that

$$R \frac{dU}{U} = \frac{d(zh)}{z\theta}, \quad (5)$$

where  $z = m/m_1$ , and is therefore the fraction of the charge burnt at any instant, and  $U \equiv V - m_1b$ , which may be called the "free volume" behind the projectile.

Again from (3) and (4) it follows that

$$m_1zh = \frac{1}{2}Mu^2, \quad (6)$$

the equation of energy, as is otherwise obvious.

It is known that any propellant when once ignited is burnt in parallel layers, so that the rate at which the thickness diminishes is, in accordance with the statement made above, given by

$$\frac{de}{dt} = f(p), \quad (7)$$

where  $e$  is the thickness burnt off from any surface in time  $t$ . According to Petavel† and Mansell‡,  $f(p)$  for cordite is equal to  $a_0 + a_1p$ . Using the values given by them, the first term is only of importance for low values of the pressure, *i.e.*, in the initial stages of the explosion, or when the densities of loading are low, when there are other factors of much more importance to be taken into consideration, so that in what follows we shall take  $f(p) = ap$  as

\* Charbonnier, *op. cit.*, pp. 9-17.

† Petavel, 'Phil. Trans.,' A, vol. 205 (1906).

‡ Mansell, 'Phil. Trans.,' A, vol. 207 (1908).

being more applicable to normal gunnery practice, leading to a considerable simplification in the mathematics of the theory. This is also taken to be the law of burning for French propellants by Charbonnier. There is, finally, the relation connecting the thickness  $e$  with the fraction  $z$  of the gas burnt off, which depends upon the geometry of the propellant, and will be discussed later.

It is of interest to consider the connection between this theory and that of Charbonnier. Taking (2) and (6), and considering the particular case in which the loss of heat contents,  $h$ , is proportional to the drop of temperature, as in (1*b*), we have, on elimination of  $h$  and  $\theta$ ,

$$\frac{1}{2}Mu^2 + \frac{f}{R}p(V - m_1b) = m_1f\theta_0z$$

which is equivalent to Charbonnier's third fundamental equation,\* differing from it only in the interpretation of the constants involved. As obtained by Charbonnier, this equation appears to be an empirical modification of the corresponding equation applying to the case when the cordite is all burnt before the projectile moves, and it is curious that it should turn out to be a special case of the theory of this paper.

#### *Derived Equations for Initial Pressure $p_0$ .*

If it were possible to obtain an expression for the resistance encountered by the projectile during the engraving of the driving band, it would not be difficult to incorporate it into the general theory of this paper, though the resulting differential equations might have to be solved arithmetically. In the absence of such an expression, the influence of the driving band may be discussed by studying the effect produced on the indicator diagram by raising the initial pressure before the projectile begins to move.†

Suppose therefore that the pressure rises to a value  $p_0$  before the projectile moves, a mass  $m_0$  of propellant having been burnt, the equation connecting these two quantities being

$$p_0 = Rm_0\theta_0/U_0$$

as in the explosion in a vessel of constant capacity  $V_0$ , where  $U_0 = V_0 - m_1b_1$  and  $V_0$  is the volume of the chamber of the gun. Taking  $f(p) = ap$ , we have from (3) and (7) on integration

$$Mu = \frac{A}{a}(e - e_0), \tag{8}$$

where  $e_0$  is the thickness burnt before the projectile moves.

\* *Op. cit.*, pp. 141, 142.

† This method has been used by Charbonnier and others.

From (6) and (8) we then have

$$zh = \frac{1}{2} \frac{A^2}{m_1 M a^2} (e - e_0)^2 = \frac{1}{2} \frac{A^2 e_1^2}{m_1 M a^2} \left( \frac{e}{e_1} - \frac{e_0}{e_1} \right)^2$$

where  $2e_1$  is the total thickness to be burnt through before the propellant is converted into gas.

Writing  $B = \frac{1}{2} A^2 e_1^2 / m_1 M a^2$  which is the fundamental constant of the theory, and putting  $y = e/e_1$ , so that  $y$  is the fraction of the thickness burnt at any time, the last equation reads

$$zh = B(y - y_0)^2. \quad (9)$$

The geometry of the propellant gives the relation between  $z$  and  $y$  in the form

$$z = \phi(y). \quad (10)$$

Finally from (5) we get

$$R \frac{dU}{U} = \frac{d(zh)}{z\theta} = \frac{2B(y - y_0) dy}{\phi(y)\chi(h)} \quad (11)$$

where we have put  $\theta = \chi(h)$ , being the general form of an equation of the type (1a), and  $h$  is further a function of  $y$  from (9) and (10).

The integration of (11) and its reduction to a form suitable for numerical calculation is the sole mathematical difficulty, and an accurate analytical result can only be obtained in very few cases. For many purposes it will be sufficient to give to the temperature  $\theta$  a mean value  $\bar{\theta}$ , which may be taken as the arithmetic means of the temperatures corresponding to the initial and final values of  $y$ . This gives an approximate integration of (11), which gives very accurate results up to the point of maximum pressure, since the variation of  $\theta$  is small compared with that of  $y$ , in the form

$$R \log(U/U_0) = \frac{2B}{\bar{\theta}} (F_1 - y_0 F_2) \quad (12)$$

where 
$$F_1(y) \equiv \int_{y_0}^y \frac{y}{\phi(y)} dy, \quad F_2(y) \equiv \int_{y_0}^y \frac{dy}{\phi(y)}.$$

The form of  $\phi(y)$  has been given for all the ordinary shapes by various writers, and is in general a cubic function of  $y$ ; (*cf.*, *e.g.*, Ingalls, 'Interior Ballistics,' and Charbonnier's work already quoted). In the case of the multi-perforated American nitro-cellulose there is a difficulty when the grain breaks up into the so-called "slivers," which are cylinders whose cross-sections are composed of arcs of circles, and it is not easy to treat these by accurate mathematics. Fortunately, in general about 85 per cent. of the charge is burnt when this break-up occurs, and approximate methods of calculation can be applied to the slivers. In order to avoid any discontinuity in the rate at which the pressure changes, the initial volume *and* surface of the slivers

should agree with the initial volume and surface of the more tractable geometrical form, by which the slivers are replaced for the purpose of the calculation. This makes  $\phi(y)$  and its differential coefficient continuous at the point where the form of the function changes.

*Maximum Pressure of Explosion.*

One of the most important results is the value of the maximum pressure, since this can be determined experimentally, and the comparison of the theoretical and experimental values is of the greatest importance in testing the theory.

By differentiating (2) and using (2) and (4), it will be found that the pressure is a maximum when

$$R \frac{d}{dz}(z\theta) = \frac{d}{dz}(zh). \quad (13)$$

This result can be simplified if we use (1*b*) instead of (1*a*) since we expect only a small drop of temperature while the charge is burning rapidly before the maximum pressure is reached. In this case the left-hand side of (13) is

$$R \frac{d}{dz} z(\theta_0 - h/f) = R\theta_0 - \frac{R}{f} \frac{d}{dz}(zh),$$

so that (13) reduces to

$$Rf\theta_0 = (R+f) \frac{d}{dz}(zh), \quad (14)$$

or finally, from (9) and (10) to

$$Rf\theta_0 \frac{d\phi}{dy} = 2B(R+f)(y-y_0). \quad (15)$$

This equation, in general a quadratic in  $y$ , having been solved, the corresponding value of  $h$  is found from (9) and (10), whence  $\theta$  can be calculated from (1*b*), while the corresponding value of  $U$  is found from (12), so that the maximum pressure is readily determined.

So far the investigation applies only up to the instant at which the cordite is all burnt. After this there is only the expansion of the whole mass of gas to be dealt with and the equation for adiabatic expansion obtained in Part I applies; but if  $h$  is used as independent variable, the equation of adiabatic expansion is from (5), since  $z$  is now unity,

$$R \frac{dU}{U} = \frac{dh}{\theta} = \frac{dh}{\chi(h)},$$

the integration of which can be readily adapted to numerical work in the case of cordite, in which  $\theta$  is given in terms of  $h$  by (1*a*).

*Results for M.D. Cordite.*

In the case of the standard British propellant, cordite, made up into cylinders assumed so long that the burning at the ends can be neglected,  $\phi(y) = 1 - y^2$ , and (15) is therefore a simple equation for the value of  $y$  at maximum pressure. The actual drop of temperature to maximum pressure can be shown to be always less than  $R\theta_0/2(R+f)$ , which in this case is  $240^\circ$ , a result which justifies the procedure by which, in the calculation of the maximum pressure,  $h$  has been taken to be a linear function of the temperature.

In this case also the integration of (11) can be carried out analytically,  $\theta$  being given in terms of  $h$  from (1a), and the value of  $\log(U_1/U_0)$  can be expressed in terms of  $B$  and  $z_0$ ,  $U_1$  being the value of  $U$  at the instant when the charge is all burnt. For practical purposes it would be necessary to tabulate  $\log(U_1/U_0)$  as a double-entry table in  $B$  and  $z_0$ , but various methods of approximate integration of (11) can be devised, which are sufficiently accurate for the purpose, and which avoid the heavy arithmetical work involved in the calculation of such a table.

As an example, the theory has been applied to the case of an 11-inch gun, using M.D. cordite, for which we may take  $m_1 = 238$  lb.,  $M = 760$  lb.,  $r_1 = 0.15$  in. The value of the constant  $a$  for the rate of burning is taken from Mansell's investigation, and is  $0.611$  in.<sup>3</sup>/Ton-sec. for the charge at  $60^\circ$  F. The initial pressures have been taken as 0, 1, and 2 Tons/in.<sup>2</sup> respectively, and the corresponding indicator diagrams are plotted in fig. 3. They show the effect of raising the initial pressure on both the maximum pressure and on the position of the projectile when the charge is all burnt. It has also, of course, a considerable influence on the total thermo-dynamical work done, which is proportional to the area under the curves, its magnitude for the three cases being 46,590, 47,710, and 48,380 foot-Tons respectively.

The value of the initial pressure,  $p_0$ , which must be taken in order to make the experimental and theoretical maximum pressures agree, depends naturally on the value of the constant  $a$  chosen as the standard, and is usually of the order of 2 to 4 Tons/in.<sup>2</sup>. The value of  $p_0$  having been chosen in this way, it is found that in the largest guns the experimental kinetic energy of the projectile is from 92 to 95 per cent. of the total energy measured in the indicator diagram.

The above statements cannot, of course, apply to all guns and to all charges; they are only approximate, but show the order of magnitude of the empirical factors, which in any form of theory have to be introduced in order

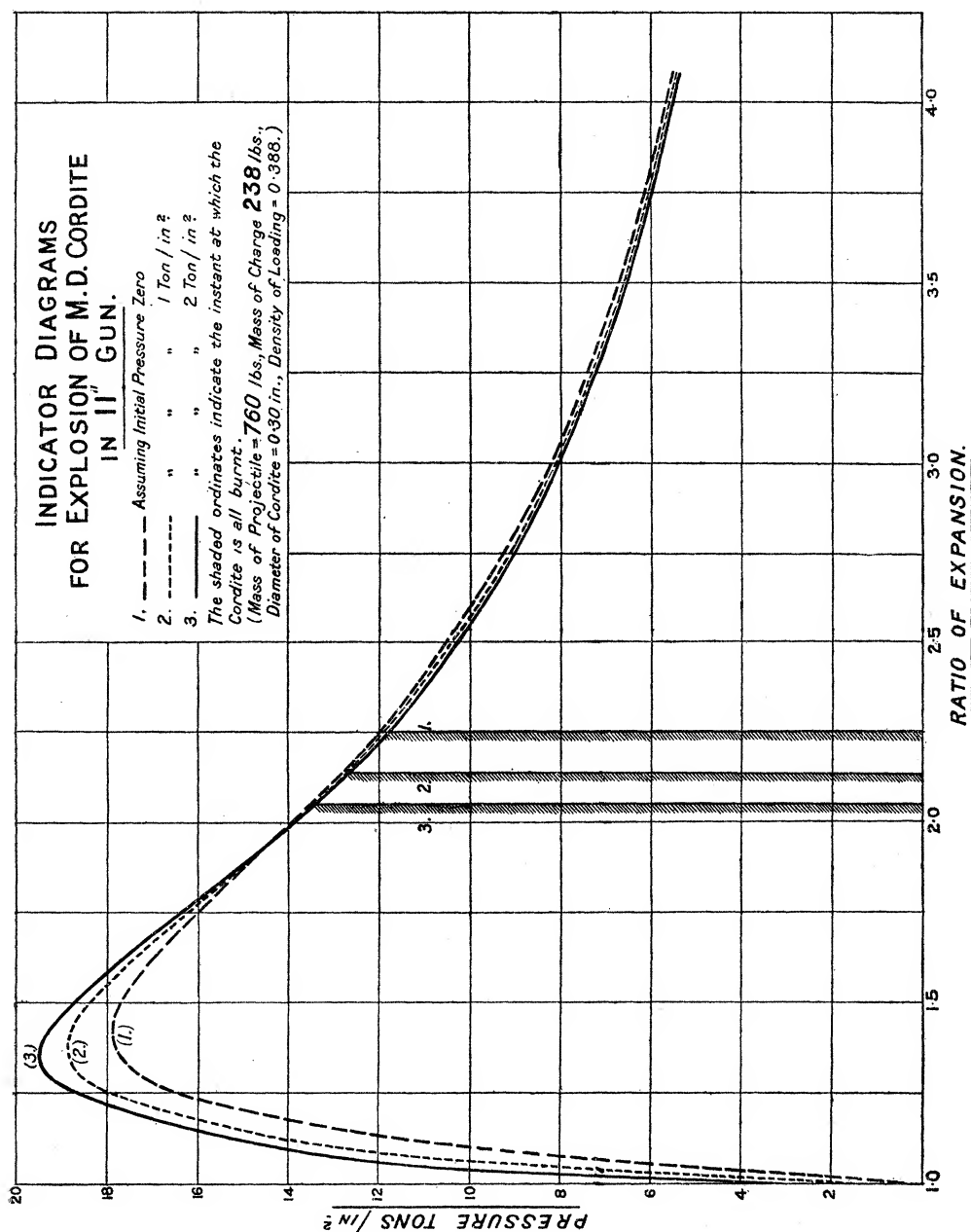


FIG. 3.

to take into account the resistance of the driving band and the losses of energy in heat and friction.

*Equations for Zero Initial Pressure.*

The equations of the theory are considerably simplified if it is assumed that the projectile begins to move directly any gas has been given off from the burning charge. The corresponding equations can easily be found by making  $y_0$  zero in (9), (11), (12), and (15), the whole course of the explosion then depending on the single parameter  $B$ .

Applied to any particular case, these equations will always give too low a maximum pressure, but they may be used with a modified interpretation so as to be of practical value. Apart from the constants in the expression for  $h$  as a function of  $\theta$ , there are two other constants,  $\theta_0$  and  $a$ , which appear in the equations. If it be assumed that the frictional force in the rifling can be allowed for by a virtual increase in the mass of the projectile, then it is a simple extension to consider all such forces which give rise to losses of energy as allowed for in this way, which is equivalent to a decrease in the fundamental constant  $B$ .

Taking the constants  $\theta_0$  and  $a$ , as determined from theoretical or experimental considerations, we can allow for all neglected losses of energy by finding in what ratio  $B$  must be diminished in order, for example, to give the correct maximum pressure. The same ratio—a coefficient of ignorance—may then be used in calculations for a similar type of gun.

This method is essentially that employed by Ingalls in his 'Interior Ballistics.' Ingalls has two disposable constants, corresponding in some ways to the  $\theta_0$  and  $a$  of this theory, and he determines them separately, so as to make the experimental and calculated values of the maximum pressure and muzzle velocity agree. These values can then be employed in future calculations with the same propellant and a similar type of gun.

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